

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) PROGRAM

Project Summaries

May 25, 2005

Cell Fabrication, Testing, and Characterization

Vince Battaglia

Lawrence Berkeley National Laboratory

In support of the BATT Program mission to bring science to the understanding and improvement of cell performance, BATT Task 1.1 is responsible for providing reproducible, low-impedance cells that have been well tested and characterized. Thus, our work is split into three subtasks.

Cell Fabrication: Several of the recommendations at the 2004 review were related to work conducted by this task. Specific comments indicated concern about cell reproducibility and contamination. Accordingly, much of our efforts during the past year were focused on trying to improve these areas. First, we completely reorganized our laboratory to make it more efficient. Then, we concentrated our efforts on cell-fabrication methods. It was clear that prior cells exhibited high impedance. Through experimentation and modeling we determined that the source of this impedance was a large contact resistance between the Al current collector and the cathode laminate. Earlier, this problem was addressed by coating the current collector with a 20-micron-thick conductive additive/polymer film. The presence of the film greatly reduced the cell impedance; however, using such a thick film was considered to be impractical, so we developed a process for coating 2-micron conductive films onto Al substrates. This new coating works as well as the old coating. We also made a number of changes to the cell-fabrication processes to reduce the possibility of water contamination. We moved the cathode materials and laminates into a glove box, added heat lamps to the laboratory fume hood, reduced the air-exposure time from 24 h to 1 h, and added two vacuum-drying steps to the cell-fabrication procedure. To demonstrate repeatability, we fabricated four cells from each laminate casting. Our latest batch of cells has just completed a specific electrochemical characterization test (ECT, see below), where they showed a 6% variation in capacity. At the end of May 2005, these cells will have just begun an aging test. The results of this test will be compared to the tests performed on an identical cell chemistry in the ATD Program.

Cell Testing: A major element of this task is to test materials for their ability to meet FreedomCAR goals. There are several goals that are specific to a given application, but they can mostly be divided into two groups: power goals and energy goals. Therefore, in collaboration with the Srinivasan/Newman group, we developed an ECT that tests cells for both power and energy capability. Since developing this test, we have applied it to pouch cells made from laminates of LiFePO_4 supplied by HQ and pouch cells made in-house from laminates of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. Analysis of cell data indicates that a 400 V battery of these laminates would consist of either 104 4.8-Ah LiFePO_4 cells or 91 5.8-Ah $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cells to meet the Power Assist goals. The analysis also shows that although such batteries would meet the power requirements, the LiFePO_4 -based cell would fall short of the available energy requirement of 500 Wh between 30 and 60% DOD by 50 Wh, whereas the $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ -based cell would exceed the available energy goal by 100 Wh. Upon completion of the aging tests, these cells will be distributed to other BATT Program PIs for cell failure analysis.

Cell and Materials Characterization: Once cells are built and tested, it is critical to understand the cell performance results by collecting physical, chemical, and electrochemical characterization data. Physical characterization to be performed by this group includes BET, PSA, and SEM. Chemical characterization includes XRD, TGA, and ARC. Electrochemical characterization will be carried out by applying the ECT and ac-impedance (EIS) to full cells with reference electrodes. To date, we have collected 70% of the SEMs and 40% of the BETs, and performed the ECT and EIS on LiFePO_4 and $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ pouch cells.

Cell Development, Overcharge Protection, Cathode Materials

Thomas J. Richardson
Lawrence Berkeley National Laboratory

This task addresses a number of issues important to the development of safe, cost-effective, Li-ion batteries with adequate energy and power densities and extended lifetimes. These include overcharge protection, general issues of component structure and stability, and exploratory work on alternative electrode materials.

Overcharge protection is an essential element of any battery system. For Li batteries, overcharging presents serious safety hazards and can dramatically shorten cell lifetimes. A reliable overcharge-protection mechanism is therefore an indispensable requirement for large cell assemblies. Ideally, this would be achieved with a minimum of added weight, volume, and cost. We have demonstrated that electroactive polymers, whose conductivity depends upon their state of charge, can provide overcharge protection in Li batteries by means of a reversible, self-actuating, resistive internal shunt that allows overcharge currents to pass through a cell while maintaining a safe cell potential, thereby preserving the cell discharge capacity and allowing the rest of the cell stack to operate normally. In FY 2004 we succeeded in protecting cells operating above 4 V at moderate current densities through the use of a bilayer separator with a high-voltage polymer in contact with the cathode and a lower-voltage polymer in contact with the anode.

In FY 2005, we have extended the range of cathode materials protected to include the lithium-rich spinel $\text{Li}_{1.05}\text{Mn}_{1.95}\text{O}_4$ at rates up to 2C, and we have shown that the mechanism works as well in a LiBOB electrolyte as with LiPF_6 . In cells containing graphite anodes, the mechanism is also effective. The anodes available to us, however, had limited cycle life and were not well matched to the cathodes. This caused the holding potentials to be greater than expected and to increase with time. This problem will be addressed in collaboration with the BATT Program Cell Development group.

Cold cells are highly susceptible to overcharging due to high resistance in the electrodes as well as in the electrolyte. In contrast to the conditions at ordinary or elevated temperatures, at which cathode and electrolyte damage are common, the primary effect of overcharging at low temperature is Li plating on the anode surface, which can lead to loss of cyclable lithium and reactive instability. Redox shuttles depend upon facile diffusion and therefore perform poorly when the electrolyte viscosity is high. The conducting polymer shunt, however, requires only a small amount of ion mobility to convert the resistive polymer to a conductive state. It can, therefore, provide overcharge protection until the electrolyte becomes solid. Because the mechanism is active only in cells that cannot accept the charge, local heating due to the resistive shunt can bring those cold cells to operating temperature faster.

A productive collaboration with the Ross group led to a publication demonstrating the occurrence and effects of anodic polymerization of the additive vinyl ethylene carbonate (VEC) on the surface of the cathode in Gen 2 cells.

Lithium-Ion Polymer Batteries with Low-Cost Materials

Karim Zaghib

Institut de Recherche d'Hydro-Québec (IREQ)

Studies on the optimization of HQ process for using water-soluble binder (WSB) for negative electrodes (natural graphite) and cathode materials (LiFePO_4) were completed. The results show that a smaller amount of WSB can be used *vs.* PVDF. We found that an optimal ratio of WSB content *vs.* the amount of solvent thinner led to an increase in the speed of the coating process. Our results showed that electrodes fabricated with WSBs yield higher performance than electrodes containing PDVF. The HQ coating process using low-cost WSB produced electrodes (graphite, LiFePO_4 and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$) with performance superior to those obtained using the conventional coating process.

Optimization studies of a new gel composed of x% polymer and (1-x)% liquid [EC-DEC- LiPF_6] showed that a 5/95 polymer/liquid ratio by weight yielded good mechanical properties. We determined that appropriate wetting conditions could be achieved by adding 3% polymer (MW 5000) to the liquid electrolyte. Hybrid UV/thermal cross-linking methods to promote gel formation were investigated.

We investigated Gen2- LiFePO_4 materials produced by Phostech, and our results showed that LiFePO_4 electrodes, cycled at 60°C *vs.* either Li, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or graphite, have very good performance: 1% capacity loss in 100 cycles when using a Li metal anode and 2% capacity loss in 50 cycles when using a natural graphite anode with LiPF_6 in EC+DEC.

Accomplishments

- Completed evaluation and safety studies of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ and low-cost LiFePO_4 cathodes in Li-ion polymer cells (First quarter, Fiscal Year 2004).
- Completed physicochemical characterization (conductivity, mechanical properties, *i.e.*, swelling, and oxidation stability) of a new gel polymer electrolyte with EC-DEC- LiPF_6 . (First quarter, FY 2004).
- Observed that 4,5-dicyano-1,2,3-triazole lithium (LiDCTA) has thermal stability similar to lithium bis(fluorosulfonyl) LiFSI , demonstrated good cycle life with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode, and found it to be not suitable when used with a graphite anode.
- Preliminary studies indicated that the compound $\text{LiMn}_{0.5}\text{Fe}_{0.5}\text{PO}_4$ give 80% of the theoretical capacity when using gel electrolyte.
- Preliminary studies indicated that Sumitomo metallized plastic is an acceptable packaging material for Li-ion polymer cells, but for long-time storage there is capacity fade when used with graphite/gel/ LiFePO_4 cells due to moisture infiltration.
- Several Li-ion gel-type cells and coin-type cells were prepared and delivered to LBNL for evaluation. In addition, positive (LiFePO_4) and negative (natural graphite) electrodes and electrolyte were sent to LBNL.
- The most-recent 20 cells performed poorly; we are aggressively working on *in situ* gel formation and sealing problems (due to moisture infiltration).

Design, Optimization, and Fabrication of Li-ion Electrodes for High-power Applications

Dean Wheeler and John Harb
Brigham Young University

This report covers the first nine months of a new experimental and modeling effort to improve the power and cycle-life performance of composite electrodes. We will make the improvements by fabricating and analyzing cathodes with novel structures and by developing new ways to evaluate the ion-transport properties of electrolytes for screening purposes.

Efforts during this period included fabrication and preliminary testing of LiFePO_4 cathodes containing new combinations of conductive carbons, in particular low-cost vapor-grown carbon fibers obtained from Pyrograf Products, Inc. Cells were assembled and tested according to BATT-Program protocols in order permit comparisons with results from other groups. The cells in which some or all of the graphite and carbon-black additives were replaced with carbon fiber showed significantly increased high-rate cell capacity and reduced impedance; cells with these compositions will be better suited for HEV applications. We are currently working toward better control of electrode thicknesses during the casting process, which is made especially difficult with fibers present in the cathode slurry. In the next several months these new fiber-containing cathodes will be tested for cycle life performance and will be shared with other BATT Program groups for additional testing and analysis.

The development of experimental and computer-simulation techniques to investigate liquid electrolyte transport properties is the second aspect of this work. During this period, we accomplished preliminary tasks toward developing usable tools for rapid screening of potential electrolytes. When subsequently completed, the molecular simulation tool will allow a first-principles estimation of transport properties of proposed electrolytes as a function of temperature and concentration. The experimental technique being developed involves a novel use of the Hall Effect to measure directly the transference number of electrolytes, a transport property that is especially difficult to measure, but that is needed to model cell performance.

Non-Carbonaceous Anodes

Michael M. Thackeray
Argonne National Laboratory

During FY2005, efforts at ANL were focused predominantly on two subtasks: 1) the investigation of a stabilized lithium product (Lectro™ Max Powder, FMC Corporation) as a prelithiating agent for non-carbonaceous anodes, and 2) rate studies of intermetallic *vs.* graphite electrodes.

Lithium Lectro™ Max Powder is stabilized by a surface coating of lithium carbonate. FMC, in collaboration with AEA Technologies in the UK, has already demonstrated the effectiveness of this powder by using it to pre-lithiate graphite anodes when fabricating charged $\text{Li}_x\text{C}_6/\text{LiV}_3\text{O}_8$ and $\text{Li}_x\text{C}_6/\text{MnO}_2$ Li-ion cells. The specific objectives of our first subtask were to evaluate the effectiveness of Lectro™ Max Powder in reducing the first-cycle capacity loss of intermetallic (Cu_6Sn_5 and Cu_2Sb) and metal oxide (SnO) electrodes, and to evaluate the differences between reactions of Lectro™ Max Powder with insertion compounds (*e.g.*, graphite and $\text{Li}_4\text{Ti}_5\text{O}_{12}$) and with compounds that operate by displacement reactions (*e.g.*, SnO and Cu_6Sn_5). A major advantage of using Lectro™ Max Powder is that the amount of lithium to be added to the electrode can be accurately controlled. To date, we have not yet significantly reduced the first-cycle capacity loss of SnO or Cu_2Sb electrodes. The conclusion from our preliminary studies is that Lectro™ Max Powder is effective for prelithiating insertion electrodes such as electronically conducting graphite that can react immediately to form Li_xC_6 , whereas electrodes that operate by displacement reactions, such as SnO , Cu_6Sn_5 and Cu_2Sb may not react readily with the powder in our present electrode design, presumably as a result of insulating surface layers, reaction kinetics and activation barriers, and particle size restrictions that may prevent the prelithiation reactions from going to completion.

The copper-based intermetallic compounds Cu_6Sn_5 and Cu_2Sb were selected for the rate studies; they were evaluated against a standard graphite (SFG10) electrode at room temperature. In addition to using copper current collectors, the effect of adding copper or silver conductive additives to the parent electrode matrix was evaluated because copper is extruded from Cu_6Sn_5 and Cu_2Sb when reacted electrochemically with lithium. In general, Cu_6Sn_5 electrodes did not cycle well when cycled over a wide potential window (2.0-0 V), nor did they provide any rate advantage over SFG10. However, Cu_6Sn_5 electrodes with an Ag additive and a smaller voltage window showed a significantly superior rate capability between a C/10 rate and a 1C rate. Cu_2Sb electrodes exhibited a slightly superior rate capability than SFG10 when cycled between 2.0 and 0.6 V. Work is in progress to monitor the effect of temperature on the rate capability of the electrodes.

Our studies on intermetallic electrodes are being complemented by NMR studies of InSb and Cu_2Sb with C. Grey to gather more information about the complex reaction mechanisms that occur during electrochemical cycling.

Collaborators who assist in this task are: Y. Gao and M. Yakovleva (FMC Corporation); and C. Grey (SUNY, Stony Brook – NMR studies).

Novel Anode Materials

M. Stanley Whittingham

SUNY at Binghamton

The goals of this project are to replace the presently used carbon anodes with safer materials that will be compatible with low-cost manganese oxide and phosphate cathodes and the associated electrolyte. Specifically we plan to gain a better understanding of what limits the use of simple alloys as the anode. The focus is being placed on tin materials, with the initial experiments being carried out on pure tin foils. We are also exploring oxides that are not poisoned by impurities from the cathode, and the impact of the electrolyte salt and solvent.

Metal-Based Anodes. The presently used graphitic carbon anode, as employed in Li-ion cells, show exceptional cyclability, but can pose safety problems under high charge rates. We are investigating some simple metals, which form alloys with lithium, to determine whether they can substitute for carbon and to gain a better understanding of their capacity loss during cycling. Our initial studies have been on tin foil, which can be used in the pure state without the complications of side reactions from other anode components. Although this tin foil cycles without loss of capacity for over 10 cycles even at rates of 3 mA/cm^2 , it then loses capacity rapidly in most cases. Reducing the dimensions to the micron level, by using expanded foils, did not remedy the loss (with K. Zaghib of HQ). We will explore using nano-size tin. All indications at present suggest that resistive SEI layers are formed on the surface, which eventually cause loss of electrical contact between the tin grains. We are working with R. Kostecki at LBNL to follow the surface behavior of the tin foil during cycling. We are also exploring the difference between using a second component that either reacts with lithium or is inert to lithium. Examples include bismuth and manganese.

Oxide-Based Anodes. We have investigated the anodic behavior of some mixed manganese-vanadium oxides, and we are expanding that study to manganese oxides based on the promising results presented on nano-sized silicon pillars and by the Amiens group of Tarascon on CoO. Specifically we are exploring forming nanosized fibers of MnO_x , and will compare them to the titanium oxide spinel anode.

LiBOB Electrolyte. We have found that the lithium in LiPF_6 and LiBOB forms a tetrahedrally coordinated $\text{Li}(\text{EC})_4$ complex in the EC/DMC mixed solvent; our study showed that only EC forms the tetrahedral complex with LiBOB [2]. This study also explained the great sensitivity of LiBOB to water, with which it forms a 1:1 adduct. Initial results using LiBOB, synthesized in our lab, show lower power capability but less capacity loss during cycling. We have now secured a commercial sample of LiBOB.

Collaborations and discussions are being held with Dr. Robert Kostecki (LBNL) and Dr. Karim Zaghib (IREQ Hydro-Quebec).

Publications:

1. Quan Fan, Peter Zavalij, and M. Stanley Whittingham, "Anode Hosts for Lithium Batteries: Revisiting Tin and Aluminum," *Mater. Res. Soc. Proc.*, 2005, 835: K6.16.
2. Peter Y. Zavalij, Shoufeng Yang, and M. Stanley Whittingham, "Structural Chemistry of New Lithium Bis(Oxalato)Borate Solvates," *Acta Cryst.*, 2004, B60: 716-724

Physical Characterization of Polymer Electrolytes

Nitash P. Balsara

Lawrence Berkeley National Laboratory

We have measured the electrical, mechanical, and morphological characteristics of a series of a poly(styrene-block-ethylene oxide) diblock copolymer PS-b-PEO systems with varying amounts of added PEO homopolymer. Characterization tools used include small-angle X ray scattering (SAXS), transmission electron microscopy (TEM), optical birefringence, and rheology. Conductivity measurements were performed on mixtures doped with small amounts of LiTFSI (EO:Li ranging from 50:1 to 15:1). The conductivity of our systems ranges from $0.5 \cdot 10^{-4}$ to $2 \cdot 10^{-4}$ S/cm. We attribute this to the formation of a continuous network of PEO channels in our system. At 80°C, the shear modulus of our polymers is 10^9 dyn/cm². The modulus of our electrolytes is thus a factor of 100 larger than that of pure PEO.

In an effort to understand the interactions of the Li⁺ ions with PEO chains, we performed small-angle neutron scattering (SANS) experiments on a series of PEO blends with a 19:1 ratio of hydrogenous PEO to deuterated PEO with varying levels of Li salts (LiTFSI and LiClO₄). All samples were prepared and sealed in airtight sample holders in a dry box to avoid any moisture contamination. Samples were analyzed for H₂O contamination after the SANS experiments using NMR, and found to be completely dry. We have established that the scattering peaks observed in our previous experiments were the result of water contamination. Our results indicate that the changes in the PEO conformation with increasing Li concentration are less than 8%.

We have begun work on the polymer electrolyte gel system. We are creating crosslinked networks of commercially available polymers/monomers that can be swollen with Li salt solutions in EC/PC/DMC mixtures. Two systems have been identified: (1) poly(acrylamidomethylpropanesulfonic acid) based gels, and (2) crosslinked PEO networks. Acrylamidomethylpropanesulfonic acid is an inexpensive monomer that is widely used in personal care products due to its biocompatibility and hydrophilicity. We have experience in making crosslinked networks of poly(AMSA) using crosslinking agents such as N-N'-methylenebis(acrylamide). We will monitor the crosslinking density to control the rheological properties of the poly(AMPSA). The H⁺ in poly(AMPSA) can easily be replaced by Li⁺ using *sec*-butyllithium, to give a single-ion conductor.

We continue to collaborate with members of the BATT program on rheological and structural characterization of polymer electrolyte systems.

Electrolytes – R&D for Advanced Lithium Batteries

John Kerr

Lawrence Berkeley National Laboratory

Work in this task has changed focus toward the behavior of polymer electrolyte gel and polyelectrolyte gel materials in response to the reviewers' comments at the 2004 annual review, as well as the need for higher rate capability for high-power applications. The postulated advantages of polymer gel electrolytes lie in potentially increased safety due to decreased volatility and reactivity as well as in cost savings for separators and cell packaging. The adhesive properties of the polymer gel may be used to hold the electrodes together, thereby eliminating the need for metal cans and applied pressure on the cell stack. Simply put, the polymer gel electrolytes need to act as a sophisticated glue that does not impede transport of lithium ions yet limits the reactivity of the other components. We have begun to examine polymers and polyelectrolytes from prior dry polymer work that now incorporate components of Li-ion liquid systems. This is a logical progression allowing us to complete work on the Li-metal/polymer systems and put to good use our accumulated experience with these polymers materials. The questions to be answered by this work are:

1. Are polymer gels safer?
Compare the chemistry and reactivity of liquid systems with the gels and dry systems. For this purpose we carry out electrochemical and thermal testing that includes DSC, ARC, and wet chemistry experiments combined with chemical analysis of the products. We use our ability to alter the chemical structures of polymers, solvents and salts to develop structure-function relationships.
2. What are the effects of gels on:
 - a. Transport properties,
 - b. Interfacial behavior, and
 - c. Calendar and cycle lifetime?
3. Can Li-metal electrodes be used with polymer gels?
To address this question we extend prior work that has been carried out on Li-metal/dry polymer systems to gel-electrolyte systems.

The use of Lewis acid salts such as LiPF_6 with dry polymer electrolytes shows that these salts are unstable and result in attack on the ether polymers under dry conditions. Aging experiments with 10% PEGDME250 and PEGDME500 added to LiPF_6 -EC/EMC (3/7) (ATD Program Gen 2 electrolyte) showed that the ethers reacted more rapidly than the EC or EMC, thereby leading to higher-molecular-weight materials that may include fluorine. GC/MS analysis of the products from these solutions and other samples from ATD Gen 2 cells show some evidence for the formation of fluoroorganophosphates. These results agree with NMR and desorption MS studies from other groups and indicate that polyether electrolytes are unsuitable for use with LiPF_6 electrolytes; however, the reactivity with LiBOB is considerably less.

The experiments with polyethers added to Li-ion electrolytes were intended to test the effect of increased viscosity on the interfacial impedance at Li-metal electrodes. We have found that many electrolyte systems exhibit severe interfacial impedances that limit their applicability.

Composite Polymer/Gel Electrolytes for Lithium and Lithium-Ion Batteries

P.S. Fedkiw, S.A. Khan, North Carolina State University; G.L. Baker, Michigan State University

We focused our efforts during FY05 in three areas: i) nanocomposite gel electrolytes consisting of Li salt + fumed silica (FS) + carbonate-containing solvents; ii) FS modified with anionic groups as a single-ion conductor; and iii) mixed molecular-weight (MW) polyethylene oxides (PEO) as solvent for FS + lithium salt gel electrolytes. We investigated BATT baseline electrolytes: LiBOB in γ -butyrolactone(GBL) + ethyl acetate (EA) + EC. Conductivity decreases and viscosity increases with EC content. Viscosity increases with LiBOB concentration, and conductivity increases with salt concentration up to 0.7 M, but beyond has no significant effect up to 1.2 M., the largest value used. FS nanoparticles form gel electrolytes in 1M LiBOB/GBL+EA+EC (1:1:0.1 wt ratio). Preliminary results show that hydrophobic FS forms a stronger gel than hydrophilic FS using the above mixture.

We continued to explore suitable gel electrolytes for BATT baseline Li-ion cell systems. We investigated liquid electrolyte 1M Li bis(perfluoroethylenesulfonyl)imide (LiBETI) in EC+PC+DMC+DEC (1:1:1:1). Chronoamperometry and linear sweep voltammetry show that an Al current collector is stable in this electrolyte up to 5.25 V. Gel electrolytes were comprised of 10 wt% fumed silica + 1M LiBETI + EC:PC:DMC:DEC (1:1:1:1) using three types of FS: A200 (hydrophilic), COK84 (hydrophilic), and R805 (hydrophobic). Gel behavior was observed for all samples; *i.e.*, the elastic modulus dominates the viscous modulus and is independent of frequency. The presence of FS results in a small decrease in conductivity. We conducted cycling studies of Li(Ni)/electrolyte/Li using 1M LiPF₆, 1M LiBETI, and 10% R805 + 1M LiBETI, all in EC:PC:DMC:DEC (1:1:1:1). The results show that FS improves the columbic efficiency and interfacial stability at room- and low temperature in the following order: 10% R805 LiBETI gel > LiBETI liquid > LiPF₆ liquid. Half-cell cycling with 1M LiBETI electrolyte using BATT baseline cathode material LiFePO₄ (Hydro-Quebec) was investigated. Both liquid and 10% R805 gel electrolytes show good capacity and cycle performance; however, 10% R805 gel shows higher efficiencies than liquid electrolyte.

We investigated three different sulfonate-modified fumed silicas as possible single-ion conductors: A200-lithium propanesulfonate (A200-LiPS), R711-poly(lithium vinylsulfonate) (R711-pLiVS), and R711-poly(lithium 2-acrylamido-2-methyl-1-propanesulfonate) (R711-pLiAMPS). These ion-conducting fumed silicas were dispersed into polyethylene glycol dimethylether (PEGdm, MW=250) with or without additional lithium salts to form gel electrolytes. Among these three fumed silicas, the highest conductivity is obtained using R711-pLiAMPS. A maximum room-temperature conductivity of $4.5 \times 10^{-6} \text{ S cm}^{-1}$ is obtained at a surface Li⁺ concentration of 4.2 nm^{-2} and a Li:O mole ratio of 1:100 (15.8 wt% filler). The maximum Li-ion transference number achieved for the same R711-pLiAMPS-based system is 0.78 at a surface Li⁺ concentration of 4.2 nm^{-2} and a Li:O mole ration of 1:20 (48.5 wt % filler). Adding Li salt to the solvent, such as lithium bis(trifluoromethylsulfonyl)imide (LiTFSI), LiBETI, LiBOB, or lithium phosphate (Li₃PO₄), increases room-temperature conductivity and interfacial stability while maintaining a relatively high Li-ion transference number.

We studied PEO gel systems, *i.e.*, P(EO)₂₀LiTFSI + 10% FS electrolytes with different mass ratios of PEO (MW=600K) to PEGdm (MW=250): 1/0, 3:1, 1:1, 1:3, and 0:1. Adding FS to the gel electrolytes inhibits dendrite formation and increases cell short-circuit time, which is correlated with improved elastic modulus. Increasing the PEO:PEGdm ratio also improves dendrite inhibition by increasing elastic modulus. Dendrite formation is more prevalent at higher temperatures.

New Battery Electrolytes Based on Lithium Fluorosulfonate and Fluorosulfonimide Salts

Stephen E. Creager, Darryl D. DesMarteau, Peter Hallac, Olt Geiculescu, Rajagopal Rama
Clemson University

BATT Program work at Clemson University during the June 2004 – May 2005 period has been focused on the synthesis and characterization of new fluorosulfonate and fluorosulfonimide salts targeted for use in high-power batteries suitable for eventual use in hybrid electric vehicles. Synthetic efforts were directed primarily at preparing ionic melts *via* attachment of lithium fluorosulfonate and fluorosulfonimide trifluorovinyl ether salts onto polyethylene glycol oligomers of variable molecular weight. These materials contain only ionic components, therefore they should be incapable of undergoing salt concentration polarization in the manner of conventional electrolytes (*i.e.* salt dissolved in solvent or polymer). The combination of high conductivity and resistance to salt concentration polarization afforded by these materials makes them good candidates for use in high-power Li batteries for which salt concentration polarization during high-rate charging/discharging is a significant factor limiting the power density.

Specific accomplishments over the reporting period in work involving lithium trifluorovinyl ether ionic melts are as follows:

- Three new lithium trifluorovinylether salts having the structures given below were synthesized and characterized.
$$\text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}_2-\text{SO}_3\text{Li} \qquad \text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}_2-\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$$
$$\text{CF}_2=\text{CF}-\text{OCF}_2\text{CF}_2-\text{SO}_2\text{N}(\text{Li})\text{SO}_2(\text{CF}_2)_4\text{SO}_2\text{N}(\text{Li})\text{SO}_2-\text{CF}_2\text{CF}_2-\text{OCF}=\text{CF}_2$$
- Ionic melts with both fluorosulfonate and fluorosulfonimide lithium salts attached to linear PEG oligomers of variable molecular weight between 300 and 2000 were prepared.
- All of the resulting materials were fully characterized with respect to structure (^1H and ^{19}F NMR spectroscopy) and ionic conductivity.
- Selected samples were characterized by thermogravimetry and scanning calorimetry
- DC polarization experiments with Li | electrolyte | Li cells, designed to look for salt concentration polarization effects in electrolytes carrying DC current, are underway.
- Abuse tolerance testing of electrolytes mixed with anode and cathode by ARC is planned in collaboration with LBNL co-workers

Other relevant project work from the reporting period is as follows:

- Several oligomeric Li salts were provided to BATT co-workers at NCSU for use in transference number measurements. This work completes studies on these oligomeric salts, and a manuscript describing their transport properties is in preparation.
- Transport data (conductivity) were provided to BATT co-workers at Utah for comparison with results from their modeling studies.
- Synthesis and characterization of a new family of aryl sulfonate and fluorosulfonimide lithium-polyether ionic melts is in progress. These compounds are expected to also exhibit high conductivity and to resist salt concentration polarization and perhaps also be especially amenable to economical high-volume synthesis.
- Synthesis of a new lithium fluorosulfonimide epoxide salt was completed. The salt did not readily undergo direct polymerization as was hoped for, but other approaches to using the compound to make single-ion conductors are being explored.

Molecular Modeling Electrolytes and Solid-Electrolyte Interphase

Grant D. Smith and Oleg Borodin

University of Utah

Poor ion transport in polymer and gel electrolytes and within solid-electrolyte interphase (SEI) layers, particularly at low temperatures, hinders development of Li-polymer and low-cost Li-ion batteries. Experimental investigation of the vast parameter space needed for optimization of lithium transport in electrolytes and SEI layers is expensive and is further complicated by a lack of fundamental understanding of cation transport - electrolyte structure relationships in these complex materials. Our research group has focused on developing tools and methodologies [molecular dynamics (MD) codes that use state-of-the-art potentials, force-field fitting tools, *etc.*] for accurate prediction of structural and transport properties of liquid electrolytes, dry and plasticized single-ion conductors, polymer electrolytes, ionic liquids, electrolyte interactions with surfaces, and understanding transport within common components of the outer SEI layer.

A new generation of quantum chemistry-based many-body polarizable potential energy functions (force fields) have been developed in our group that allow reliable prediction of structural, thermodynamic, and transport properties of a vast number of electrolytes from MD simulations. These simulations were used to gain fundamental understanding of cation transport in a number of previously synthesized electrolytes as well as novel electrolytes that have not been synthesized, thus, guiding experimental efforts.

Long (20 ns) simulations of PEO-based comb-branched electrolytes doped with LiTFSI revealed a number of salient features of lithium transport in them. In particular, lithium cations exhibited very fast jumps (within 0.1 ns) from one side-chain to another, and the cations not complexed by the backbone atoms tend to move faster than those complexed by the polymer backbone. Finally, cation transport was found only weakly coupled to backbone relaxation. These observations suggest that novel comb-branch polymers with a stiff backbone that does not complex cations and flexible side-chains that complex Li^+ cations are promising for use as of novel electrolytes with improved transport and mechanical properties.

Investigation of dry single-ion conductors based upon comb-branched polymers with TFSI anions attached to side chains (PEPETFSI-Li) indicated that increasing the side-chain length of comb branches is a better strategy for improving cation transport than addition of a number of short side chains. Plasticizing these single-ion conductors with EC significantly reduced the temperature dependence of the single-ion conductor conductivity, yielding promising plasticized single-ion conductors with extrapolated conductivities above 0.1 mS/cm at room temperature (plasticizer weight fraction=37 wt%). Ongoing MD simulations of single-ion conductors plasticized with pentaglyme revealed that even higher lithium transport at 423 and 393 K could be achieved due to further decoupling of lithium transport from slow dynamics of the polymer host.

MD simulations of a common SEI material, dilithium ethylene dicarbonate (Li_2EDC), predicted dramatically stronger temperature dependence of Li_2EDC compared to liquid electrolytes such as EC/LiTFSI, thereby suggesting that the outer SEI layer resistance could have a significant contribution to overall battery resistance at low temperatures.

Free energy barriers for a Li^+ cation approaching neutral surface from the liquid electrolyte EC/LiTFSI, the dry single-ion conductor PEPETFSI-Li, and the plasticized gel electrolyte PEPETFSI-Li/EC were obtained from MD simulations. The lowest barrier was found for EC/LiTFSI whereas the highest barrier was obtained for the dry single-ion conductor, indicating the higher interfacial resistance of single-ion conductors compared to those of liquid electrolytes.

Novel Cathode Materials
Michael M. Thackeray
Argonne National Laboratory

During FY 2005, our efforts continued to exploit the concept of ‘composite’ structures with a high manganese content in an endeavor to develop novel, low cost, high-energy and high-power electrodes. The concept of composite electrode structures is not new, *per se*; γ - MnO_2 , which consists of intergrown β - MnO_2 and ramsdellite- MnO_2 domains, is well known for its application in primary 1.5 V alkaline and 3 V lithium cells; the β - MnO_2 domains provide structural stability for the electrochemically active ramsdellite- MnO_2 domains. We have adopted a similar approach by using Li_2MnO_3 , which is structurally compatible with layered LiMO_2 compounds ($\text{M}=\text{Mn, Ni, Co}$), as a stabilizing component in composite $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ electrode structures. The performance goal is to achieve 200 mAh/g for 100 cycles, when charged and discharged between 4.8 and 3.0 V, without compromising the power capability of the electrode. Lithium half cells with $0.3\text{Li}_2\text{MnO}_3 \bullet 0.7\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrodes have shown that a steady capacity of 230 mAh/g can be achieved from the electrodes when cycled in cells at 50°C; slightly higher capacities are achieved at room temperature. Indications are that the performance of the BATT-selected cathode chemistry ‘ $\text{LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$ ’ can be improved by the inclusion of some Li_2MnO_3 in a composite $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMn}_{0.33}\text{Ni}_{0.33}\text{Co}_{0.33}\text{O}_2$ electrode structure.

The compatibility of close-packed layered (Li_2MnO_3) and spinel (LiM_2O_4) structures allows the concept of composite ‘layered-layered’ electrodes to be extended to composite ‘layered-spinel’ systems. In this case, our strategy is to use the layered component predominantly to provide the electrode with high capacity and to use the spinel component predominantly to provide a high-rate capability. For our initial studies, we have investigated the $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{Li}_4\text{Mn}_5\text{O}_{12}$ system in which the manganese moieties are all tetravalent. This electrode can be activated electrochemically by charging it to high potentials (>4.5 V). Data from lithium half cells, cycled over a wide voltage window (5.0-2.0 V), show that despite some capacity fade (which is not surprising for unsubstituted lithium-manganese-oxide electrodes), reversible capacities >200 mAh/g can be achieved. The data also suggest that the spinel component stabilizes the layered component and *vice-versa*. Future improvements in the electrochemical properties of composite ‘layered-spinel’ electrode structures can be anticipated by cation substitution and by control of the voltage window and the manganese oxidation state at full discharge.

‘Layered-layered’ and ‘layered-spinel’ composite electrode structures open the door to much future research and electrode optimization. Our plan in FY 2006 is to continue to evaluate the electrochemical properties of composite electrodes as a function of: 1) cation substitution; 2) full cell performance (vs. graphite and intermetallic anodes); 3) low-temperature behavior; 4) first-cycle irreversible capacity loss; and 5) stability with respect to electrolytes. Collaborators who assist in the characterization of these materials are: S. Hackney (Michigan Technological University - HRTEM studies); C. Grey (SUNY, Stony Brook – NMR studies); M Anderson (University of Wisconsin – surface coatings); P. Bruce (University of St. Andrews, UK – *in situ* neutron diffraction); and W. David (Rutherford Appleton Laboratory, UK – pdf analyses).

Novel Cathode Materials

M. Stanley Whittingham, SUNY at Binghamton

The primary goals of this project are to find (a) lower-cost and higher-capacity cathodes, exceeding 200 mAh/g, and (b) high-rate HEV compatible cathodes, both of which are based on environmentally benign materials. The major efforts are being focused on stabilized layered manganese dioxides, and on building a baseline cathode system using LiFePO_4 against which the manganese and other cathodes will be compared.

Lithium Iron Phosphate. Lithium iron phosphate is a low-cost and higher-stability cathode material with potential application in large-scale systems. In 2003/2005 our study was completed on lithium iron phosphate as a baseline system. LiFePO_4 is a stable cathode material above 1.5 volts, and cycles exceptionally well; its capacity may be enhanced to $\sim 100\%$ by either raising the temperature or lowering the power output. However, low-cost manufacturing methods needed. We have renewed our investigation of a low-temperature hydrothermal approach, wherein pure single-phase material is formed in the temperature range 180-200°C. Several vanadium and iron phosphates have also been studied; some of these have slightly higher capacities, others have enhanced rate capabilities or higher operating potentials but so far none have an overall advantage over the olivine phase.

Stabilized Layered Manganese Dioxides. The layered $\text{Li}_{1+x}\text{Ni}_y\text{Mn}_y\text{Co}_{1-2y}\text{O}_2$ system has been studied for $0.33 \leq y \leq 0.5$ to determine the optimum composition, the nature of the electrochemically active specie, the role of cobalt, and to compare capabilities against LiFePO_4 .

- We have found that some nickel in the lithium layer is advantageous, preventing phase change during cycling, and thus enhancing cycle capacity retention. Both *ex-situ* and *in-situ* experiments at BNL have been completed and are now being analyzed.
- Over 100 cycles can be obtained in either LiPF_6 or LiBOB based electrolytes; however, capacity retention is lower when the temperature is raised to 60°C with LiPF_6 .
- Increasing the charging voltage from 4.2 to 4.6 volts initially increased the capacity, but upon extended cycling all the samples had essentially the same capacity.
- The composition $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ gave the best capacity even though it contained some nickel in the lithium layer, exceeding 180 mAh/g for 20 cycles. Reducing the cobalt content by 50%, showed comparable performance but with slightly higher polarization. Increasing the formation temperature significantly reduced the surface area. Extensive cycling under partial discharge conditions (HEV cycle) will be performed in the next year, and the manganese content will be increased.

δ -Phase Vanadium Oxides. These oxides show the largest capacities but poor capacity retention at high rates. In 2005 we will finish work on $\text{NH}_4\text{V}_4\text{O}_{10}$, which shows low polarization.

Collaborations and discussions have been held with Dr. W-S Yoon (BNL), and with NIST (Neutron Diffraction experiments).

Publications:

1. M.S. Whittingham, "Lithium Batteries and Cathode Materials," *Chemical Reviews*, 2004, **104**, 4271-4301.
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3. Yanning Song, Peter Y. Zavalij, Natasha A. Chernova, and M. Stanley Whittingham, "Synthesis, Crystal Structure, Electrochemical and Magnetic Study of New Iron (III) Hydroxyl-Phosphates, Isostructural with Lipscombite," *Chem. Mater.*, 2005, 17: 1139-1147.
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Synthesis and Characterization of Cathode Materials for Rechargeable Li and Li-Ion Batteries

Marca M. Doeff
Lawrence Berkeley National Laboratory

Prior work at LBNL indicates that the performance of LiFePO_4 cathode materials is closely correlated to the structure of the *in situ* carbon (carbon coating), as determined by Raman microprobe spectroscopy (Kostecki, diagnostics task). Lower D/G (disordered/graphene) structures are associated with higher electronic conductivity, and allow more LiFePO_4 to be utilized at moderate to high rates. Work during the last fiscal year was focused on optimizing the structure of the carbon produced during synthesis of LiFePO_4 . Some carbon is formed from decomposition of the acetate or oxalate precursors used during synthesis. Addition of organic compounds or polymers prior to final calcination modifies the structure of the *in situ* carbon, but may actually result in poorer electrode performance if the additives do not decompose completely. Best results are obtained when about 4-8 wt/% volatile, easily decomposed, pyromellitic acid (PA) is added, although the amount of *in situ* carbon increases only slightly. A further improvement in carbon structure and electrode performance is obtained when graphitization catalysts such as ferrocene or iron nitrate are also added. Ferrocene is more desirable than iron nitrate because any excess is expected to evaporate without leaving a potentially troublesome iron-containing residue on particle surfaces. Carbon coating the aluminum current collector on the cathode side further increases the cell rate capability. The high-rate utilization of electrodes made with LiFePO_4 processed with ferrocene and PA is projected to be among the best of currently available materials (Srinivasan, modeling). A milestone to determine the best ratios of PA and iron promoter for optimization of the carbon coating was achieved on time. During the next fiscal year, effort will be directed toward decreasing the primary particle size and narrowing the particle size distribution to improve overall performance.

Electrochemical testing of layered O_2/O_3 $\text{Li}_x\text{Al}_y\text{Mn}_{1-y}\text{O}_2$ intergrowths was also completed. Materials that showed the best overall performance in terms of capacity, stability against spinel conversion, cycling behavior, and rate capability are intergrowths containing 12-18% Al (milestone achieved).

Experiments designed to determine the extent of Mn dissolution from various manganese oxide structures (layered, tunnel, romanechite, *etc.*) were initiated. Less Mn dissolves from O_2 structures than from intergrowths or O_3 structures, and the cycling behavior at 55°C reflects this. These experiments are now being extended to tunnel compounds. More abuse-tolerance experiments will be designed to determine the thermal stability of these compounds in charged and partially discharged states. A milestone to recommend the most abuse-tolerant manganese oxides by 09/05 has been postponed due to the magnitude of the work involved.

Conducting polymer cathodes combined with iron redox couples for lithium batteries

Kyu-Sung Park, John B. Goodenough, Steen B. Schougaard
The University of Texas at Austin

In order to enhance specific capacity and rate capability of the cathode of a lithium rechargeable battery, electrochemically active conducting polymer was combined with iron redox couples. First, we attached ferrocene groups that contain the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple onto pyrrole to form [(ferrocenyl)amidopropyl]pyrrole (FAPP) by chemical reaction, and then obtained a copolymer with 50:50 pyrrole and FAPP by electrochemical deposition. By binding redox couples to polypyrrole chains, the specific capacity of the polypyrrole is enhanced and the charge/discharge potential is flattened at the potential of the redox couple. With ferrocene, the discharge potential is flattened at 3.5 V vs. Li/Li^+ and the specific capacity is about 65 mAh g^{-1} . Because it was not possible to attach a higher concentration of ferrocene molecules to the polymer chain, the specific capacity is too low. Therefore, we physically attached an oxide to the conducting polymer. We chose LiFePO_4 as the oxide, and replaced the carbon black and PTFE of a conventional cathode with polypyrrole. The thus-obtained composite cathode shows a better specific capacity (132 mAh g^{-1} at the rate of C/5) and a reduced overpotential. Furthermore, rate capabilities are improved greatly. According to our results, replacing the electrochemically inactive additives (carbon black and PTFE) of a conventional cathode by an electrochemically active polymer is a promising way to improve the performance of a LiFePO_4 cathode. This strategy is applicable to other polypyrrole/oxide composites, *e.g.* $\text{LiNi}_{2/3}\text{Mn}_{1/3}\text{O}_2$, which contains no cobalt.

Cathodes - Superior Capacity Retention, High-Rate Spinel Manganese Oxide Compositions

Arumugam Manthiram, University of Texas at Austin

Spinel manganese oxide cathodes offer the important advantages of low cost and high rate capability compared to other systems, but exhibit capacity fade at elevated temperatures. In order to develop a firm understanding of the factors influencing capacity fade, we have been focusing on the structure-composition-performance relationships of several cation- and anion-substituted Mn oxide spinel compositions. Doubly and triply substituted compositions such as $\text{LiMn}_{2-x-y}\text{Li}_x\text{Ni}_y\text{O}_4$ and $\text{LiMn}_{2-x-y-z}\text{Li}_x\text{Ni}_y\text{M}'_z\text{O}_4$ ($\text{M} = \text{Al}, \text{Mg}, \text{Cu}, \text{and Zn}$) with $(x + y + z) < 0.15$ exhibit a combination of superior capacity retention, high rate capability, and excellent storage characteristics compared to unsubstituted LiMn_2O_4 or singly substituted compositions such as $\text{LiMn}_{2-x}\text{Li}_x\text{O}_4$ and $\text{LiMn}_{2-x}\text{M}_x\text{O}_4$. The excellent performance characteristics of multi-cation-substituted samples are due to a smaller lattice parameter difference Δa between the two cubic phases formed during the charge-discharge process and the consequent low microstrain. Characterization of cycled cathodes by micro-Raman spectroscopy in collaboration with the University of Puerto Rico (R. Katiyar) shows that the reversibility of the second cubic phase ($F\bar{4}3m$) formed during cycling to the original cubic phase ($Fd\bar{3}m$) becomes difficult as LiMn_2O_4 is cycled, as compared to $\text{LiMn}_{1.88}\text{Li}_{0.06}\text{Ni}_{0.06}\text{O}_4$, which is consistent with the correlation of capacity fade to lattice parameter difference. Although multi-cationic substitution leads to excellent performance, it results in lower capacities of < 105 mAh/g. With an aim to increase capacity without sacrificing other performance factors, we have begun to focus on the substitution of fluorine for oxygen. Fluorine-substituted oxyfluoride compositions such as $\text{LiMn}_{2-x-y}\text{Li}_x\text{Ni}_y\text{O}_{4-z}\text{F}_z$ indeed exhibit higher capacity than the corresponding oxide analogs, with a further improvement in cyclability. For example, $\text{LiMn}_{1.9}\text{Li}_{0.05}\text{Ni}_{0.05}\text{O}_{3.8}\text{F}_{0.2}$ exhibits ~ 115 mAh/g with capacity fade $< 3\%$ at 60°C . More importantly, the oxyfluoride compositions exhibit less Mn dissolution (1.5-2.0%) than the corresponding oxide compositions (2.5-3.0%), possibly due to stronger metal-fluorine bonds. Thus fluorine substitution may be an effective way to overcome the critical problem of Mn dissolution and reduce Mn spinel capacity fade in Li-ion cells. In January 2005 we supplied a cation-substituted oxide to LBNL for evaluation, and our future work will focus on optimizing oxyfluoride compositions evaluating them in Li-ion cells.

Using the knowledge gained with the 4 V spinel cathodes, we have also investigated the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ spinel, which exhibits high capacity at ~ 5 V involving the $\text{Ni}^{2+/3+}$ and $\text{Ni}^{3+/4+}$ redox couples. Similar to the 4 V system, cation-substituted $\text{LiMn}_{1.5-y}\text{Ni}_{0.5-z}\text{M}_{y+z}\text{O}_4$ ($\text{M} = \text{Li}, \text{Mg}, \text{Fe}, \text{Co}, \text{and Zn}$) compositions exhibit better cyclability and rate capability compared to the unsubstituted $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. For example, $\text{LiMn}_{1.5}\text{Ni}_{0.42}\text{Zn}_{0.08}\text{O}_4$ exhibits a capacity fade of $< 2\%$ after 50 cycles with 125 mAh/g compared to 8% fade and 130 mAh/g for $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. Also, $\text{LiMn}_{1.42}\text{Ni}_{0.42}\text{Zn}_{0.16}\text{O}_4$ retains $\sim 90\%$ of its capacity upon going from C/10 to 4C rate compared to $\sim 80\%$ for $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$. The 5 V spinel cathodes also exhibit a clear relationship between electrochemical performance and the lattice parameter difference among the three cubic phases formed during the charge-discharge process similar to the 4 V system. Our future work will focus on fluorine substitution in the 5 V system as well (consisting of other transition metals like Fe, Co, and Cu) to reduce Mn dissolution and further improve the performance.

We have found that the measurement of chemical Li extraction rates using the oxidizer NO_2BF_4 can be an effective and faster way to determine the relative Li-ion diffusion rate, which profoundly influences the rate capability. For example, the chemical Li extraction rate decreases with increasing cation disorder between the Li and transition metal planes in the layered $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ cathodes, resulting in a decrease in the rate capability.

Publications: Four journal articles have been accepted for publication this year.

Diagnostics - Electrode Surface Layers

Robert Kostecki
Lawrence Berkeley National Laboratory

We previously determined that improved electrochemical properties of LiFePO_4 are associated with a larger ratio of sp^2 -coordinated carbon, which exhibits better electronic conductivity than disordered and/or sp^3 -coordinated carbonaceous materials (collaboration with Marca Doeff, Task 4.3). However, the *in situ* carbon coating of LiFePO_4 by simple pyrolysis of organic precursors at temperatures below 800°C does not produce graphite-like conductive carbon. During the past year, our first objective was to improve the high-rate performance of composite cathodes by direct *in situ* microwave-assisted synthesis of a graphitic carbon matrix.

Microwave treatment of SFG-6 graphite/organic polymer (1:4 by weight) precursor mixtures in an ambient-pressure Ar-plasma at 600W for 3 min produced carbons that displayed a higher level of crystallinity than the original SFG-6 graphite. Their Raman spectral signatures were typically identical to that of highly oriented pyrolyzed graphite (HOPG). Organic thin-film precursors microwaved in a low-pressure Ar plasma (1-2 mTorr) at 300-1000 W for 5 s to 3 min produced highly crystalline graphitic carbons of a consistent graphene domain size. Interactions with low-pressure Ar-plasma and strong electromagnetic radiation led to vaporization and immediate pyrolysis of the organic precursor at relatively low temperatures. Direct microwave-assisted carbon coating of LiFePO_4 powders at 500 W for 30 s produced a thin layer (< 100 nm) of graphitic carbon. The carbon coating consisted of densely packed ~ 50 nm primary particles. Excellent electronic conductivity of these carbon coatings and consequent improved high-power performance of LiFePO_4 is expected. The electrochemical performance of carbon-coated LiFePO_4 powders will be investigated in the near future.

Our second objective was to investigate the effect of electrode pre-treatment on the evolution of interfacial impedance of electrodes stored in electrolyte at 45°C . In collaboration with Vince Battaglia (Task 1.1) we prepared Al/carbon black, $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ composite electrodes. Three sets of electrodes were dried under vacuum at 120°C for 6, 12, and 42 hours, respectively. These electrodes were then stored in 1.2M LiPF_6 + EC:EMC (3:7 by volume) electrolyte at open-circuit potential and 45°C in a glove box. The electrochemical impedance of the electrodes was monitored periodically during storage. *Ex situ* diagnostic analyses were carried out after the tests. We found that prolonged heat treatment under vacuum reduced significantly electrode impedance. Importantly, the electrode heat pre-treatment time determined the rate of the impedance increase upon aging at elevated temperatures. The behavior of the carbon additive contributed significantly to the impedance characteristics of the composite electrodes. SEM images of aged electrodes revealed surface deposits and morphology changes. The surface residues displayed strong fluorescence. However, Raman and FTIR were not sensitive enough to characterize these compounds. EDX surface analysis of the aged electrodes revealed that the surface decomposition products, which include most likely LiF and $(\text{LiPO}_x)_n$, originate from LiPF_6 decomposition. Oxygen and water adsorbed on the carbon black and graphite additives, as well as -C-O-H and -C=O surface functional groups, catalyze and/or react with the electrolyte. Surface reaction products create electronic and ionic barriers in the composite electrode, which contribute to the impedance rise of the composite electrodes.

Battery Materials: Structure and Characterization

Won-Sub Yoon and Xiao-Qing Yang

Brookhaven National Laboratory

The primary objective of this task is to develop and apply advanced diagnostic techniques to determine the contributions of electrode material changes, interfacial phenomena, and electrolyte decomposition to cell capacity, power decline, and abuse tolerance. The results of these studies will be used to guide the exploratory research for new cathode, anode, and electrolyte materials for high-power rechargeable lithium batteries.

We have continued *in situ* time-resolved XRD studies to monitor temperature-induced structural changes in carbon-coated LiFePO_4 provided by Dr. Zaghbi of Hydro-Quebec. The structure of the charged $\text{Li}_{1-x}\text{FePO}_4$ cathode is much more thermally stable than that of layered LiNiMnO_2 . Quite interesting temperature-induced structural changes were observed in LiFePO_4 . These changes were recently observed and correctly interpreted as temperature-driven solid solution phenomena by Masquelier's group. Our studies show that the temperature-driven solid solution is much clearer in the cathode when electrolyte is present. The electrolyte accelerates the thermal decomposition of the charged cathode material. As the degree of Li-ion deintercalation increases, the thermal decomposition takes place at lower temperature.

Soft X-ray (200 eV to 1000 eV) absorption spectroscopy (XAS) at the O K-edge and the metal L-edges, in both the fluorescence yield (FY) and the partial electron yield (PEY) mode, has been used to probe the electronic structure of $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$. Significant differences in Ni L_{II,III}-edge XAS spectra for nickel-based layered compounds at various x values were observed by comparing data collected using PEY mode with FY modes. In the case of $\text{Li}_{1-x}\text{Co}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, Ni^{2+} ions at the surface are oxidized mostly to Ni^{3+} whereas Ni^{2+} ions in the bulk are oxidized further to Ni^{4+} . This difference between the surface and the bulk becomes even larger in $\text{Li}_{1-x}\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_2$, where the Ni ions remain at Ni^{2+} state at the end of charge. It is concluded that the more nickel content in the materials, the more severe difference between the surface and the bulk.

P and Fe K-edge XAS experiments were performed for $\text{Li}_{1-x}\text{Fe}_{1-y}\text{Co}_y\text{PO}_4$ electrodes at different x values. The major charge compensation during Li deintercalation is achieved by the oxidation of Fe^{2+} ions at lower potential (~3.6 V) and the oxidation of Co^{2+} ions at higher potential (~5.0 V). A pre-edge peak was not observed in the P K-edge XAS spectrum for the pristine LiFePO_4 . However, upon Li deintercalation, pre-edge peaks begin to appear in the lower-energy region of the main edge and increase their intensities. This result shows that these pre-edge peaks originate from the hybridization of P 3p states with the Fe 3d states through a superexchange interaction. It is very interesting to note that such hybridization could occur in spite of the presence of oxygen atoms that separate phosphorus from iron.

Additional *in situ* XRD studies on spinel LiMn_2O_4 electrodes during cycling at elevated temperatures have been completed. It is notable that the capacity fading and the amount of residue structures increase with increasing cycling temperature and charge cut-off voltage. However, if the tris(pentafluorophenyl) borane (TPFPB) compound is added to the electrolyte, this problem can be reduced. After solvent washing the cathode obtained from a disassembled cell, in which significant fading had occurred, its capacity could be partially restored, and the amounts of residues were reduced. This demonstrated that the decomposition of the electrolyte and the interaction between the cathode and the electrolyte are important factors for the capacity fading of spinel cathode materials.

Diagnostics, Interfacial, and Reactivity Studies

Philip N. Ross

Lawrence Berkeley National Laboratory

The low temperature (LT) performance of Li-ion batteries is receiving increasing attention. Graphite anodes have been identified as the limiting electrode in LT performance. Along with other phenomena, Li deposition during charging at LT is believed to be responsible for permanent loss of capacity. We studied graphite anodes (MAG-10) in two electrolytes: 1.2 M $\text{LiPF}_6/\text{EC}:\text{EMC}$ (3:7 w/w) [denoted as electrolyte A, identical to ATD Program Gen 2 electrolyte] and 1M $\text{LiPF}_6/\text{EC}:\text{PC}:\text{DMC}$ (1:1:3 w/w/w) [denoted as electrolyte B] by combining hybrid pulse power characterization (HPPC) and Fourier Transform Infrared (FTIR) spectroscopy. We established differences in composition of SEI layer on graphite versus metallic Li anodes in electrolyte A. We also found compelling direct spectroscopic evidence for Li deposition on graphite anodes in electrolyte A during HPPC testing at -30°C .

Graphite anodes were assembled into Li/graphite half-cells in two electrolytes and subjected to two galvanostatic charge/discharge formation cycles at C/25. Prior to HPPC tests, anodes formed at room temperature (RT) were fully intercalated and then deintercalated to 50% depth of discharge (DOD) at C/25. We modified the RT HPPC test protocol by decreasing the pulse current and duration to avoid cell degradation and access Li deposition during charging (intercalation) at LT. First a 10 s discharging pulse at 1.5 mA cm^{-2} (1 C rate) was applied to the cells. After a 32 s rest period, a 2 s charging pulse at 0.3 mA cm^{-2} (C/5) was applied. Immediately upon completion of the charging pulse, the DOD of the cells was then increased by 5% at 0.15 mA cm^{-2} (C/10). This sequence, separated by one-hour rest periods to allow cells to return to an equilibrium condition, was repeated until the final potential reached 1 V vs. Li/Li^+ . The rates used in HPPC tests were based on the 2nd de-intercalation capacity in the formation cycle at RT.

Although both cells showed very similar voltage profiles at 30°C , cell A exhibited much higher resistance and polarization than cell B at -30°C . During a 2 s C/5 charging pulse, the voltage of cell A dropped far below -0.2 V , while that of cell B reached only -0.02 V . The polarization during the charging pulse in electrolyte A was three times large than in electrolyte B at -30°C . To gain insight into the consequence of large polarization at LT, we further characterized graphite anodes subjected to HPPC tests by FTIR spectroscopy. The FTIR spectra of graphite anodes in electrolyte A after HPPC at 30°C and -30°C reveal very different surface film compositions. While there is no spectroscopic evidence of Li deposition on graphite anodes in electrolyte B, a strong peak at 1640 cm^{-1} characteristic of the SEI on metallic Li appears on the graphite anode after HPPC tests in electrolyte A at -30°C . We further established by FTIR spectroscopy that the larger polarization and consequent Li deposition in electrolyte A are not due to differences in the SEI layers formed in those two electrolytes, *i.e.*, the SEI layers have identical compositions and thicknesses.

First Principles Calculations and NMR Spectroscopy of Cathode Materials

Clare Grey (SUNY Stony Brook) and Gerbrand Ceder (MIT)

We have continued our combined modeling and experimental work on the $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ systems, with particular focus on the structure and rate capability of the **$\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$** end member as a potential Co-free replacement for the **$\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$** system. First principles computations have suggested a structure for this material and we have now been able to confirm that structure with TEM on well-annealed samples. In addition, we have found a significant effect of processing on the performance of these materials. Through our combination of modeling and various characterization techniques, the charge/discharge behavior is now reasonably well understood. All $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ materials have about 8-10% Li in the transition metal layer, and we now understand that this "disorder" is a structural component, due to the very stable LiMn_6 moieties that form. NMR as well as computations give clear evidence that this Li in the transition metal is removed early during the charge. This creates empty tetrahedral sites which capture Li. It was predicted that this Li could be removed only at very high potential, and this has now been observed with NMR on samples charged to various potentials. Hence, the Li in the transition metal layer indirectly reduces the practical cycling capacity that can be obtained at reasonable potentials. We believe that this result is relevant more broadly to the class of $\text{Li}(\text{Ni,Mn,Co})\text{O}_2$ materials and are currently investigating the effect of this tetrahedral Li on the rate capability of the material.

Using, NMR, TEM, and XRD we found surprisingly large structural changes in the material, after only a few cycles. While the host crystal structure is retained, significant transition metal ion disorder is found in cycled samples. Following cycling between 2.5 V and 4.6 V, the local structure as probed by Li NMR changes slowly and the concentration of Li in the transition metal layers drops gradually, so that by 20 cycles no Li in the TM layers remains. The long-range structure (as probed by XRD) changes more rapidly and by 2-3 cycles, there is very little evidence for longer-range ordering in the TM layers. Similar results are seen for the $\text{Li}(\text{Ni}_{1/2}\text{Mn}_{1/2})\text{O}_2$ and $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{5/9}\text{Li}_{1/9})\text{O}_2$ materials. This indicates some mobility of the transition metal component. These changes are reflected in the potential profile and depend on the synthesis conditions of the material. Currently, we are combining NMR, XRD, TEM, and first principles modeling to develop a structural model for the changes in this material upon cycling.

Our theoretical efforts to predict electronic and ionic conductivity in electrode materials (and hence rate capability) are coming to fruition. A new *ab-initio* method was developed to calculate polaron barriers in materials such as LiFePO_4 . We also found that conductivity is also hampered by the significant association energy between the hole carrier in LiFePO_4 and the Li vacancy that creates it. In addition we have started to test a methodology for predicting the oxygen release of electrodes at high states of charge as this will become a part of our BATT project in the next fiscal year.

Corrosion of Aluminum Current Collectors

Xueyuan Zhang and Thomas M. Devine, Lawrence Berkeley National Laboratory

Our efforts during the past year were focused on four topics: the mechanism of crevice corrosion of Al current collectors; the identity of the passive film formed on Al in electrolytes with LiPF_6 ; investigation of Al corrosion behavior in electrolytes with LiBOB; and remedial actions against crevice corrosion of Al current collectors, including their effects on cell capacity.

We had earlier determined that Al current-collector corrosion was a form of crevice corrosion, called underdeposit corrosion, which occurred where Al was exposed to electrolyte at pores in the cathode. This year we investigated Al crevice corrosion using grooved polyethylene disks as crevice formers. Interestingly, Al was not corroded beneath polyethylene crevices, which suggests that microporous cathode crevices are not inert in the corrosion sense (as are polyethylene crevices), but instead increase solution corrosivity in pores. To assess the validity of this hypothesis, we proposed the idea that cathodes increase local water concentration in the pore electrolyte, thereby forming HF *via* LiPF_6 hydrolysis, and the locally high HF concentration corrodes the Al. To test this idea, we first determined that dilute concentrations of HF are highly corrosive to Al in aqueous solutions; just 0.002M HF in water destroyed the air-formed oxide film that is responsible for Al corrosion resistance. A possible source of water in the cathode is its binder, PVdF, which was found to contain 890 ppm water. Further tests indicated that up to 4,000 ppm water added to 1:1 EC:DMC + 1M LiPF_6 did not increase Al corrosion. We now plan to determine if the cathode active material increases electrolyte corrosivity by catalyzing solvent oxidation, thereby forming oxidative decomposition products are corrosive to Al.

We evaluated four possible remedial actions for improving Al corrosion resistance. In addition, we determined the effect of each remedial action on cell capacity. First, a one- μm -thick anodized layer (Al_2O_3) was found to improve the resistance of Al to uniform corrosion, but the anodized layer reduced the cell capacity to zero. Future work will determine the effect of much thinner (1-5 nm) anodized layers. Second, we discovered that a 1-nm AlF_3 coating markedly improved Al corrosion resistance, particularly in LiTFSI-containing electrolyte, and did not reduce the cell capacity. In the absence of the thin AlF_3 coating, Al was severely corroded in this electrolyte. Future work will evaluate the crevice-corrosion resistance of Al protected by a 1-nm AlF_3 layer. Third, removal of the air-formed oxide on Al was found to not adversely affect Al resistance to uniform corrosion in 1:1 EC:DMC + 1M LiPF_6 . Anodic polarization formed a protective AlF_3 layer, and removal of the air-formed oxide increased the cell capacity from 140 to 160 $\text{mA}\cdot\text{hr}/\text{cm}^2$. Future work will determine if removal of the air-formed oxide impairs Al crevice-corrosion resistance. Fourth, we determined that Al purity had little effect on its resistance to uniform corrosion in 1:1 EC:DMC + 1M LiPF_6 . However, increasing the Al purity increased the cell capacity. In the future we will investigate the effect of Al purity on its resistance to crevice corrosion when coated with a microporous cathode.

Our third major effort determined the identity of the protective passive film that forms on Al in LiPF_6 -containing electrolyte. Other investigators (using XPS) reported that Al was protected by AlF_3 , however this conclusion has been disputed. We used a combination of CV, EQCM, EIS, and XPS to convincingly demonstrate that Al is protected by a duplex film that consists of an inner layer of air-formed oxide and an outer layer of AlF_3 . The AlF_3 thickness was controlled by the applied potential during anodic polarization (5.5V forms a 1- nm AlF_3 layer).

Finally, we investigated the corrosion behavior of Al in 1:1 EC:DMC + 1M LiBOB. The as-formed passive film was the most protective we have studied, and was also able to protect Al in LiTFSI-containing electrolyte. In fact, Al was completely resistant to pitting corrosion in 1:1 EC:DMC with a mixed salt of 9:1 LiTFSI:LiBOB.

Performance and Failure in Lithium-ion Batteries

John Newman

University of California Berkeley, Lawrence Berkeley National Laboratory

Particle Expansion and Fracture

We have accomplished our fracture-modeling milestone, to determine stress distributions in electrode materials during lithium insertion/extraction. Results indicate that graphite particles are likely to fracture at high charge and discharge rates typical of hybrid-electric vehicles (HEVs). Choosing a small particle size minimizes these effects. The stress also increases with the degree of volume expansion, and decreases with increasing diffusion coefficient.

Refinements to the model include the influence of nonidealities in the solid solution upon the electrode kinetics and thermodynamic factor. Lithium insertion and extraction under potentiostatic and galvanostatic conditions have been successfully simulated with the model. Nonidealities embodied in the thermodynamic factor and, under potentiostatic conditions, the exchange current density have a significant impact on the charge and discharge behavior, including the stress response. The variation of stress due to that in the thermodynamic factor may be especially important when considering material fatigue due to strain cycling. Because the stress depends upon the state of charge (SOC) of the electrode, there may be an optimum cycling range, corresponding to high solid-state diffusivity, for HEVs

Capacity Fade: Cyclable Lithium and Active Material Loss

We have carried out zero-dimensional thermodynamic simulations to elucidate the differences and commonalities of cyclable lithium loss and active material loss. We have explored various possible cycle paths using the framework of an SOC operating window. Specifically, we have examined a possible mechanism involving continuous cracking and reformation of the SEI due to volume changes in lithium-insertion compounds. We have compared this to a hypothetical case in which equivalent capacity fade occurs due to active material loss in the positive electrode. In both cases, assembly of the cell with excess positive electrode capacity should prolong cell life, but may lead to undesirable lithium deposition at high rates (as in HEVs) when active material loss is the mechanism for capacity fade.

Comparison of High-potential Anodes with Graphite

We have generated a Ragone curve for a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /Gen 2 spinel cell to compare with that of a graphite/Gen 2 spinel cell (see Srinivasan's work). The specific energy of the former is considerably lower than that of the latter at low rates, but provides an improvement for high rates ($> 30\text{C}$). An important advantage of a high-potential anode over graphite is the reduced propensity for SEI formation, lithium deposition, and other possible side reactions. This system should be explored further for use in HEVs.

Transport Property Measurement

The development of an anion-reversible electrode has continued for LiPF_6 electrolytes of interest. This reference electrode will be used in EMF measurements in order to independently determine activity coefficients. These measurements will enable a more accurate determination of the transference number as a function of electrolyte concentration in these systems. Transference-number measurements, when combined with remaining transport property data, will allow for comparison between different electrolytic solutions.

Modeling of BATT Program Baseline Chemistries

Venkat Srinivasan and John Newman
Lawrence Berkeley National Laboratory

The goal of this project is to understand the behavior of the three BATT baseline systems, namely, LiFePO_4 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (L333), and LiMn_2O_4 (spinel), vs. graphite, when used under EV and HEV conditions. We achieve this goal by performing lab-scale experiments and translating their behavior to batteries by using theoretical developments. We have used this approach in three task areas this year:

Comparing various Li-ion chemistries: We are continuing the task of using a model-based approach to compare the performance of the BATT baselines to each other and to the DOE EV and HEV goals. The procedure involves (i) developing a mechanistic model for the chemistry, (ii) performing half-cell thermodynamic and rate experiments, (iii) comparing the model to the experiments to extract unknown parameters, and (iv) performing optimization to understand the behavior under EV and HEV operating conditions. This optimization is performed by maximizing the specific energy for a specified time of discharge. We have now completed this study for five different systems, namely, the three baselines with a graphite negative electrode, and the L333 and $\text{LiV}_6\text{O}_{13}$ cathodes with a Li-metal negative electrode covered with a single-ion conducting glass. The comparison shows that spinel is the best chemistry for high-power applications, although all three baselines show promise for use in HEVs. However, none of the graphite-based cells is close to achieving the EV goals. It appears that Li-metal based systems would be required to achieve the energy densities needed to bring EVs to the marketplace. We will extend this study to Li-S cells and cells with alloy anodes.

Modeling HEV operation of batteries: In response to reviewer suggestions that we extend our optimization studies to address HEVs specifically, we have chosen the graphite/spinel system as an example, followed the Freedom CAR HEV protocol, and identified the limitations that decrease performance. This allows us to minimize the limitations using cell design changes and thereby identify the optimum design and SOC of operation. We plan on extending this analysis to the two other baselines.

Fast Charge and Path-dependence in LiFePO_4 : Evidence exists that it is possible to achieve fast-charging with LiFePO_4 . For example, experiments suggest that while 70 mAh/g is lost when discharging at a 3C rate, only 15 mAh/g is lost on charge. We believe that this feature is caused by the shell-core juxtaposition of the two phases, whereby transport on discharge occurs in LiFePO_4 while on charge transport occurs in FePO_4 . Evidence exists that these two materials are different in their barriers for electron motion. We have used our model along with the experimental data to extract the diffusion coefficient in the two materials. The analysis suggests that diffusion in FePO_4 is six times larger than that in LiFePO_4 .

The shell-core juxtaposition also suggests that the behavior of this system should have a history dependence. For example, an electrode brought to 50% SOC from a fully-discharged state would have a different shell-core configuration than one brought to the same SOC from a fully-charged state. Interestingly, if one were to start from this 50% SOC point and then perform either a charge (or discharge), the movement of the phases would depend on the configuration at the start of the charge (or discharge). We have experimentally observed this history dependence as a difference in utilization when polarizing the cell at high rates (*e.g.*, 3C) from 50% SOC. We are in the process of trying to understand this phenomenon better.

Modeling and Experimentation-Electrochemical Materials

A.M. Sastry
University of Michigan

Both the addition of conductive additives and the compression of Li-ion electrodes during cell manufacture have been shown to improve cyclability and electronic conductivity for high-power applications. In this project year, we have developed new simulations to model conductivity of the particle networks within both anodes and cathodes. In our studies on electronic conductivity, we experimentally examined LiFePO_4 cathodes and graphite anodes (Gen 2) with varying amounts of carbon additives. Prior conduction experiments (four-point probe) on graphite anodes showed that the resistivity decreases from 176 to 67 $\Omega\cdot\text{cm}$ as the amount of carbon black increased from 3 wt% to 10 wt%. More importantly, electrical conductivity of the anode without compression was increased by a factor of 38 with the addition of a carbon coating around the graphite (14 wt%).

However, excessive compression has been shown experimentally to reduce conductivity, putatively due to the breakage of particles. In this project year, a mechanics model was developed and implemented, allowing detailed investigation of induced stresses among compacted particles, during the application of compressive loads on electrodes. Using data collected using atomic force microscopy (AFM) in our lab, we first characterized particle shape distributions in electrodes manufactured by other BATT workers (Striebel, Zaghib). A dynamic collision model was then developed to generate realistic morphologies of composite electrodes. Then, a commercial finite element analysis package was used to analyze the stress distributions within the particles themselves. Simulation results showed substantial local deformation occurs once the particles are compressed to a “jamming” fraction 58% (random packing of ellipsoidal particles). The force required to pack the particles to a prescribed volume fraction during manufacturing can be predicted *via* simulation. Both the simulation results and the decreased post-packing conductivity in experiments indicate that a pressure greater than 200 kg/cm^2 (200 MPa) can cause breakage in particle materials in SL-20 electrodes. Interfacial friction reduces this jamming fraction by as much as 7% (from 58% to 51%). The coefficient of friction was determined to be approximately 0.1; this value can be used in prediction of external loading and internal stresses under other conditions.

Our ultimate objective is to use our mechanics simulations, in conjunction with electrochemical simulations of performance, to simultaneously account for the effects of particle shapes and sizes in simultaneously mapping mechanical, conductive, and electrochemical responses of electrodes. In close collaboration with other workers (Srinivasan and Newman), a 3D finite element model has been proposed and is under development to simulate the electrochemical performance of the $\text{Li}/\text{LiPF}_6+\text{EC}:\text{DEC}/\text{LiFePO}_4$ system. This new simulation is capable of incorporating realistic particle morphology in modeling of cell performance. Preliminary results on single particles produce expected behavior, and low-density networks have been generated and are being studied.

We have now established that particle morphology plays a significant role in electrochemical conductivity of other the relevant BATT Program electrochemistries, due to the size of particles used for conduction relative to electrode thickness. Our next steps include investigation of the relationship between electrode particle shapes on power and energy capabilities of composite LiFePO_4 cathodes, and seamless incorporation of mechanics models in the same FE implementations. We further aim to work closely with other BATT workers in testing and simulations of new materials, using these combined approaches.